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Detecting initial aragonite and calcite variations in limestone–marl alternations

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ABSTRACT

Limestone–marl alternations are commonly used for high-resolution cyclostratigraphic studies and palaeoenvironmental reconstructions, but diagenetic studies indicate that not all limestone–marl alternations reflect genuine differences in the initial sediment composition driven by environmental changes. Differences in the ratios of diagenetically inert trace elements between limestones and marls indicate changes affecting the terrigenous fraction of the precursor sediment. Contrarily, limestone–marl alternations without these differences can be the product of: (i) variations in CaCO_3 input (aragonite, calcite); (ii) distortion of the latter by diagenetic CaCO_3 redistribution; or (iii) diagenetic CaCO_3 redistribution in a homogeneous precursor sediment. The aim of this study is to provide a method to differentiate these cases and to identify variations in the proportion of calcite and aragonite in the precursor sediment composition. The model of differential diagenesis assumes that the concentration of diagenetically inert elements is inversely proportional to the amount of redistributed CaCO_3 . Consequently, the difference between ratios of diagenetically inert elements from two adjacent beds is a measure for CaCO_3 redistribution. This is quantifiable by the vector length between ratios from two adjacent beds. The approach is illustrated here by evaluation of a case study from the Silurian of Gotland, Sweden. Trace elements were compared according to their solubility during diagenesis. All elements bound to clay minerals or calcite show similar patterns of vector length, while vector length of elements which fit into the aragonite lattice, and are diagenetically mobile, differ. The vector length approach provides a tool to test the diagenetic origin of limestone–marl alternations, to identify initial variations in CaCO_3 input and to test a limestone–marl alternation's suitability for cyclostratigraphic analyses.

Keywords Aragonite, calcite, carbonate sedimentology, limestone–marl alternation, palaeoenvironmental reconstruction.

INTRODUCTION

Limestone–marl alternations

Rhythmically alternating carbonate lithologies, or limestone–marl alternations (LMA), are commonly interpreted as a record of periodic environmental changes forced by for example Milankovitch cycles (e.g. Bellanca *et al.*, 1996; Batenburg *et al.*, 2012). Limestone–marl alternation occurrences range from marginal marine to marine and from shallow to deep depositional settings, and are developed from well-bedded to nodular, from carbonate dominated to marl dominated, and from thick-bedded to thin-bedded (see compilation in Westphal *et al.*, 2008). Nevertheless, their common trait is the alternation usually between two states: relatively CaCO_3 -rich (limestone) and relatively less CaCO_3 -rich (marl) independent of their absolute CaCO_3 content. The precursor sediment of limestones and marls consists of terrigenous material (quartz and clay), biogenic calcium carbonate (calcite and/or aragonite) and organic matter. Changes in the sedimentary input of LMA precursor sediments can be caused by, for example, changes in productivity such as of calcareous plankton, or changes in material transport from carbonate factories (Seibold, 1952; Flügel & Fenninger, 1966; Einsele, 1982; Arthur *et al.*, 1984; Pittet & Strasser, 1998; Wendler *et al.*, 2002). Changes in the depositional environment can, but need not necessarily be cyclic (Puetz *et al.*, 2016). To record changes in the depositional environment – cyclic or not – at least one compound of an LMA precursor sediment needs to be sensitive to the environmental change (Einsele, 1982; Beltran *et al.*, 2007). Furthermore, while linkages to astronomically forced climate change are well-established in several cases (e.g. Batenburg *et al.*, 2012; Martinez, 2018), diagenetic processes can enhance, disguise, or even introduce rhythmicity to the sediment (Bathurst, 1971; Hallam, 1986; Ricken, 1986; Munnecke & Samtleben, 1996; Melim *et al.*, 2002; Westphal, 2006; Nohl & Munnecke, 2019).

Shallow diagenetic alteration of the precursor sediment

The transformation from a loose precursor sediment to a lithified rock involves pervasive alteration associated with shallow diagenesis (some authors also refer to it as ‘early’ diagenesis). It takes place in the loose sediment shortly after

deposition but could take place as deep as 170 m, as suggested by studies on pore water gradients (for example, International Ocean Discovery Program – IODP – site 1461, Gallagher *et al.*, 2017; Egger *et al.*, 2018). It involves an intense mass exchange with at least a major CaCO_3 import at one site, as well as a major CaCO_3 export from close proximity. It may lead to the differentiation into two lithologies which often do not follow original sedimentary structures and sometimes even cross-cut them (Bathurst, 1971; Munnecke & Samtleben, 1996; Westphal *et al.*, 2015; Nohl & Munnecke, 2019). The possibility of diagenetic differentiation into two lithologies entirely through a diagenetic pathway therefore puts in question the reliability: (i) of the lithological rhythmicity (e.g. Kent, 1936; Sujkowski, 1958; Hallam, 1964, 1986; Westphal *et al.*, 2015; Nohl & Munnecke, 2019; Nohl *et al.*, 2020); and (ii) of environmental proxies which are subject to diagenetic alteration or are concentrated or diluted by CaCO_3 redistribution (e.g. Munnecke & Samtleben, 1996; Westphal & Munnecke, 2003; Westphal, 2006; Nohl *et al.*, 2019; Su *et al.*, 2020).

Westphal *et al.* (2010) assessed the suitability of LMA for cyclostratigraphic studies. Indications of a primary signal in a given LMA can, for example, be (partially) established on a structural level, by examining sedimentary structures (such as infilled burrows across different lithologies), variations in ratio between clay composition and diagenetically inert elements or different (micro-)fossil assemblages in the marl and limestones, respectively (Nohl *et al.*, 2019). Well-constrained independent age constraints might further inform a judgement regarding the astronomical origin of a particular LMA.

Deep (also called ‘late’) diagenetic carbonate dissolution and reprecipitation may enhance sedimentary differences (Eder, 1982; Ricken, 1986). Nonetheless, a deep diagenetic LMA origin is incompatible with several phenomena, for example: (i) uncompacted limestone, as pressure dissolution of calcite as source for cementation implies a certain degree of compaction; and (ii) separation of bioturbated sediments into well-bedded limestones and marls by sharp boundaries (Westphal, 2006). Munnecke & Samtleben (1996) thus argue for aragonite dissolution and reprecipitation as calcite cement during early burial; in that model, the precursor sediment (composed of terrigenous material, calcite and aragonite) experiences aragonite dissolution in the shallow subsurface, associated with sulphate reduction or methanogenesis

(De Lange *et al.*, 1994; Munnecke, 1997; Krumins *et al.*, 2013; Jordan *et al.*, 2015). The mature limestone consists of its original calcite and terrigenous fraction, as well as the imported secondary calcite from aragonite dissolution. The marl, in contrast, retains only its original calcite and terrigenous fraction. The source of aragonite, however, is under debate: some authors presented molluscs as an important source of aragonite (Cherns & Wright, 2000; Wheeley *et al.*, 2008), others considered aragonitic skeletal grains and mud more broadly (Munnecke, 1997; Nohl & Munnecke, 2019). Nevertheless, this CaCO_3 redistribution can enhance or disguise primary environmental signals, or even introduce rhythmicity to a previously homogeneous precursor sediment. Differential diagenesis, thus, can affect parameters such as magnetic susceptibility or absolute concentrations of trace elements. Westphal *et al.* (2008) argued, if the ratio of diagenetically inert trace elements such as Ti/Al shows clear differences between limestones and marls, the LMA can be geochemically identified as a product of environmental changes which affected the terrigenous compound of the precursor sediment. If the ratio of diagenetically inert trace elements (for example, Ti/Al) is constant, only the carbonate fraction of the precursor sediment, composed of terrigenous material, aragonite and calcite, could have varied due to environmental changes. However, no method of differentiating between: (i) variations in CaCO_3 input (aragonite, calcite); (ii) distortion of the latter by diagenetic CaCO_3 redistribution; and (iii) diagenetic CaCO_3 redistribution in a homogeneous precursor sediment (also referred to as diagenetic dilemma; Westphal *et al.*, 2008), has been available up to now. The main objective of this manuscript is the identification of variations in aragonite and calcite input.

NOVEL APPROACH TO IDENTIFYING VARIATIONS IN ARAGONITE AND CALCITE INPUT

Without variation in the composition of terrigenous material, the ratio of diagenetically inert trace elements such as Ti/Al is constant (Westphal *et al.*, 2008; Nohl *et al.*, 2019). The trace element concentration is diluted (limestone) or condensed (marl) by CaCO_3 redistribution (Fig. 1). Based on these two well-documented observations, it follows that a constant element ratio will be also retained across a succession where aragonite or calcite input in the precursor

sediment varied. This theoretical prediction has been corroborated empirically (Westphal *et al.*, 2008, 2010; Amberg *et al.*, 2016).

To obtain information about (non-)variations of calcite and aragonite in the precursor sediment, the vector length (VL) or distance between the trace element ratios of two adjacent beds (Fig. 1) is introduced in this study and calculated as:

$$\text{VL} = |\overrightarrow{LM}| = \sqrt{(M_{\text{Al}} - L_{\text{Al}})^2 + (M_y - L_y)^2} \quad (1)$$

where \overrightarrow{LM} is the vector between the ratio of aluminium (Al) and element y in limestone (L) and the ratio in the adjacent marl (M).

The VL quantifies the distance between the concentration of element ratios in the mature lithology (i.e. limestones and marls) as an absolute value and is thus a measure of CaCO_3 redistribution. A variation in VL results from varying input of aragonite, calcite, or both. The following cases 0 to IV explain the possible patterns in VL, CaCO_3 content in limestone and CaCO_3 content in marls from variations in aragonite, calcite, terrigenous material, and combinations of these three constituents as illustrated in Fig. 2. The cases I to IV are idealized endpoints of the spectrum of possible individual intermediate states, which depend on absolute and relative concentrations in the three main constituents: aragonite, calcite and terrigenous material.

- *Case 0:* LMA with primary variations in the composition of terrigenous material is identified by different ratios of diagenetically inert elements.
- *Case I:* In LMA of purely diagenetic origin from a homogeneous precursor sediment the condensation or dilution of diagenetically inert elements will not vary between beds as the amount of redistributed CaCO_3 is constant. Thus, the VL are constant as well as the CaCO_3 content in limestones and marls.
- *Case II:* Stable input of calcite and terrigenous material leads to stable CaCO_3 content in marls. Variations in aragonite input concentrate or dilute the ratio of diagenetically inert elements and, thus, alter the VL. The VL are proportional to the aragonite input.
- *Case III:* Variations in calcite input lead to inverse variations in CaCO_3 and VL. The proportion of aragonite and terrigenous material, and thus the VL, decrease with increased calcite input.

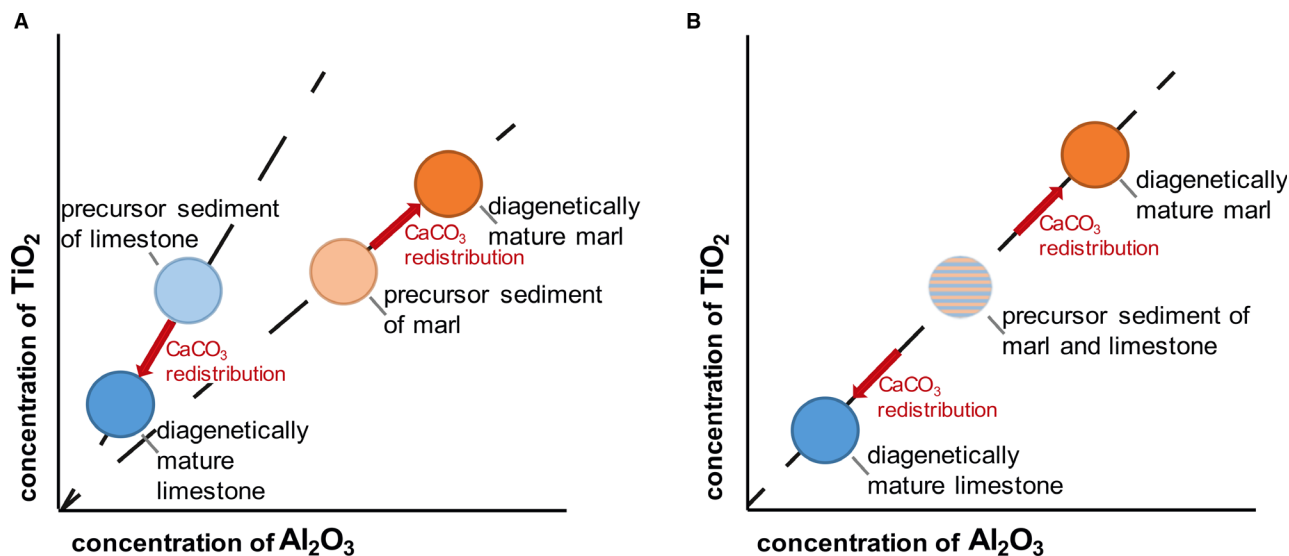


Fig. 1. (A) Limestone–marl alternations (LMA) with differences in the composition of terrigenous material show different $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios for limestones and marls. They can be clearly linked to environmental changes despite CaCO_3 redistribution. (B) LMA without differences in the composition of terrigenous material (T) show the same $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio for limestones and marls. The vector length VL between the ratios of two adjacent beds is a measure for CaCO_3 redistribution.

- *Case IV:* Variations in aragonite and calcite input lead to variations in CaCO_3 content in marls and limestones and in VL. As both aragonite and calcite input change, the variations in VL and CaCO_3 contents are less intense than in case II and case III.

Testing the vector length approach

Aragonite and calcite have similar chemical formulas, but their crystal systems differ. Thus, some elements can be incorporated into the aragonite or calcite lattice, or both, depending on the ion's radius. After aragonite dissolution, not all of its trace elements can be incorporated into calcite cement. This is further limited by the element's ionic potential which determines its solubility (Railsback, 2006) depending on the redox conditions during precipitation (Thomson *et al.*, 1993; De Lange *et al.*, 1994; Railsback, 2003, 2006). Trace elements were grouped by their source (aragonite, calcite, clay, incompatible or unassigned elements) and their solubility in reducing conditions (Table 1; Railsback, 2006). The VL approach is supported if elements which fit into the aragonite lattice are differentially preserved compared to stable constituents (for example, TiO_2). In contrast, all elements from calcite or clay minerals should have similar variations in

VL, independent of their solubility. The VL of elements ascribed to 'incompatible or unassigned' will depend on their solubility.

CASE STUDY

A continuous section with 37 limestone–marl couplets with a total height of 11.34 m was sampled bed-wise at Lickershamn (57°49'39.2"N, 18°30'25.9"E) on Gotland (Sweden). The exceptionally well-preserved strata on Gotland comprise an almost 450 m thick succession of Silurian carbonates, ranging from Telychian to Ludfordian age (Jeppsson, 1983; Riding & Watts, 1991; Munnecke, 1997; Calner *et al.*, 2004). They were deposited in an epicontinental tropical sea at the margins of the Baltic Shield (Laufeld & Bassett, 1991; Munnecke, 1997). The strata, which dip towards the southeast at an angle of 1°, lack evidence of tectonic deformation (Calner *et al.*, 2004). The studied samples belong to the Sheinwoodian Höglint Formation. The Höglint Formation is formed of large bioherms and patch reefs (Calner *et al.*, 2004). The reefal structures are surrounded by crinoid limestones which interfinger with LMA (Munnecke, 1997). The outcrop near Lickershamn is a small stream gully that caves upstream into the Höglint Formation. The distal Höglint Formation is

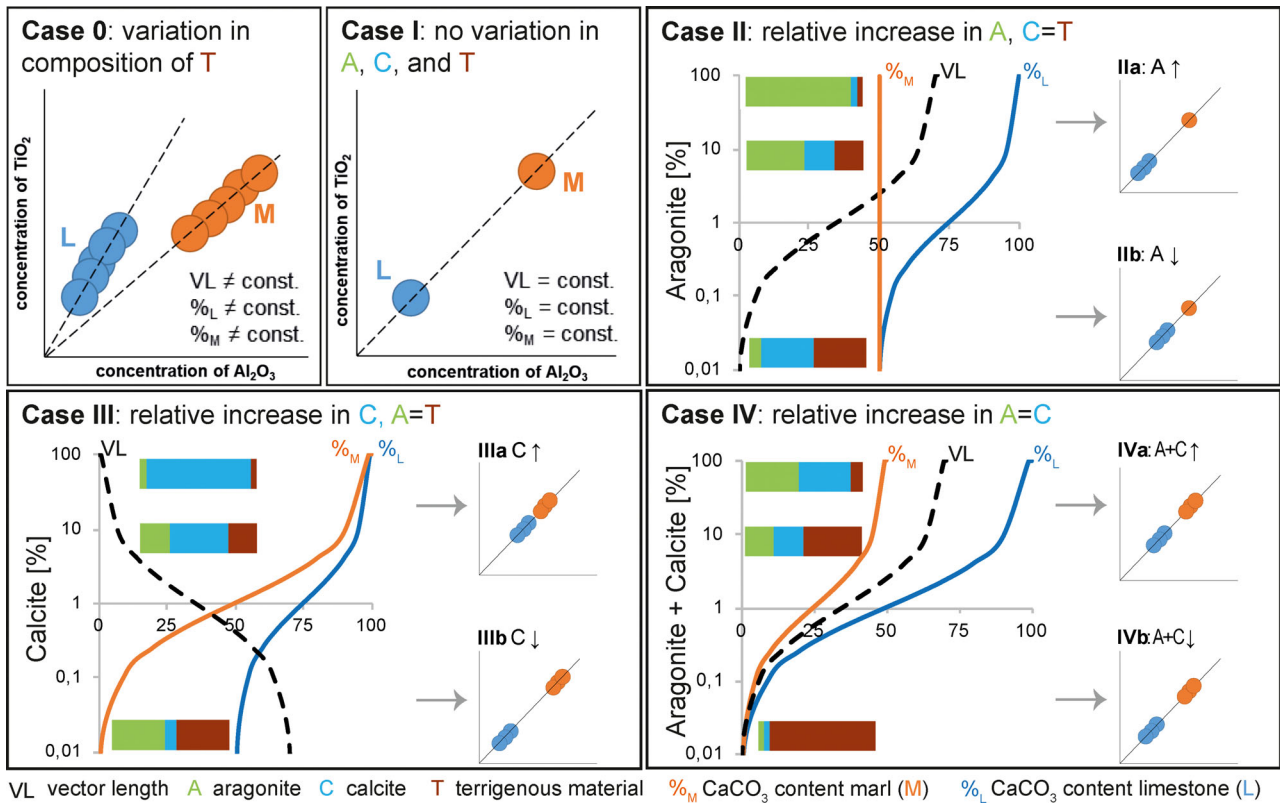


Fig. 2. Theoretical cases 0 to IV and their influence on vector length (VL) and CaCO₃ content in limestones and marls. The large x–y plots in cases II to IV show the results from theoretical data modelling how VL and CaCO₃ contents in marl and limestone change with variations in the respective precursor sediment compound (aragonite, calcite, terrigenous material). The small x–y plots with orange (marl) and blue (limestone) dots show for cases I to IV theoretical changes in the ratios of, for example, Ti/Al concentrations which increase or decrease the VL dependent on the original sediment composition and the amount of aragonite redistributed or indicate in case 0 an environmental signal affecting the terrigenous compound of the precursor sediment. The illustrated cases represent endmembers of numerous possible combinations of sediment composition and the variation of its compounds.

Table 1. Overview of elements and their solubility in reducing conditions (extracted from Railsback, 2003, 2006).

Category	Aragonite	Calcite	Clay	Incompatible or unassigned
Insoluble (ionic potential >3.5 and <8.5)	Pb	Fe ₂ O ₃ , MnO	P ₂ O ₅ , SiO ₂ , Al ₂ O ₃ , TiO ₂ , MnO	V, Nb, Ga, Cr, Th
Soluble (ionic potential <3.5 or >8.5)	Zn, CaO, Sr, Ba	Zn, CaO, MgO	MgO, Na ₂ O, Ba, K ₂ O	Y, Zr, Rb

developed there as well-bedded LMA with alternating thickness which can be followed laterally over several hundreds of metres. It was deposited in a calm, marine deep shelf environment and displays few skeletal grains, although their proportion slightly increases towards the top of the

formation. The carbonate content increases too and is in line with previous interpretations that this interval represents a shallowing upward sequence (Munnecke, 1997; Watts & Riding, 2000). The skeletal grains comprise mainly fragments of stromatoporoids, tabulate corals,

molluscs, ostracods, crinoids, trilobites and brachiopods (Munnecke, 1997). It compares to the transition from the Ireviken Member to the Brissund Member described for the 'Höglint limestone Formation' in Riding & Watts (1991) for which a water depth of about 40 m is interpreted. This succession was selected because of its exceptional preservation, the lack of tectonic deformation, its lateral undisturbed continuity and its pronounced rhythmicity.

METHODS

The trace element distribution from 75 samples was determined by X-ray fluorescence (XRF) analyses with a SPECTRO XEPOS diffractometer (SPECTRO Analytical Instruments GmbH, Kleve, Germany). The bulk rock composition was examined in fused beads made from the middle part of each sample which was ground in an agate disc mill. Before, the loss of ignition was determined by heating 1.00 g of the dried, ground sample with 4.83 g lithium borate for 24 h. The weight percentage of oxides of major elements, and the concentration in ppm of trace elements were quantified and are in the rest of the text referred to as elements. The standard deviation was determined from 10 measurements of a limestone standard and is <0.03 wt.% and, except for Ba (5.6 ppm) and Sr (2.6 ppm), it is below 1.5 ppm. The same ground samples were used for gasometric determination of the CaCO_3 content by reaction with 10% hydrochloric acid in a carbonate bomb (error: 0.5%). The results of the measurements as well as the determination of standard deviation are available via the link provided following the *Conclusions*.

Element ratios

Trace elements are compared to Al (Calvert & Pedersen, 1993; Tribouvillat *et al.*, 2006). The ratio between each trace element and Al_2O_3 was calculated for each bed and the values were compared for marls and limestones. Goodness of fit was measured using Spearman's rank correlation to be consistent with further analyses (Fig. 3A). These and all following analyses were conducted in R Software version 3.4.4 (R Core Team, 2018).

Quantification of vector lengths

The VL between ratios of Al_2O_3 and other elements was calculated as described in Eq. 1 for

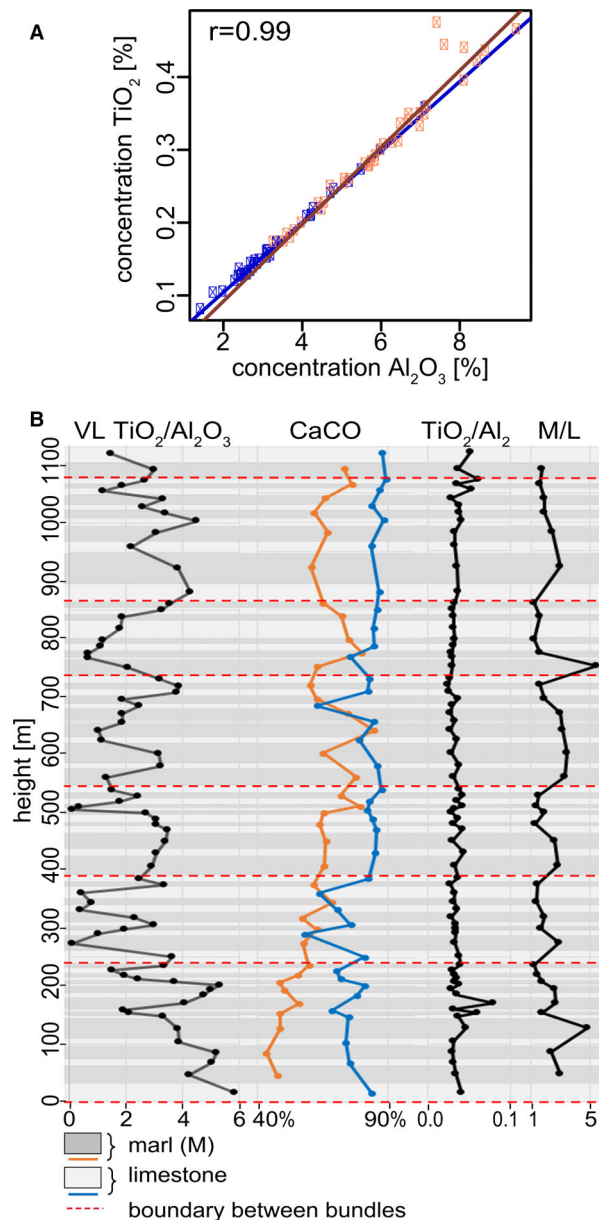


Fig. 3. (A) Relationship between the ratio of TiO_2 (vertical axes) with Al_2O_3 (horizontal axis) shown for marl (orange) and limestone (blue). Trend lines are fitted using linear regression. (B) Comparison of vector length (VL), CaCO_3 content, $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratio and thickness ratio between limestone and marl. In the background the limestone–marl alternation is indicated in grey lines representing the original bed thickness, thus the curves are stretched to bed thickness. The red dashed lines indicate bundles based on observed variations in bed thickness.

each couplet. Similarities in the vector length patterns of trace elements were explored using a principal component analysis (PCA) following

Legendre & Legendre (2012) as implemented in the R package *vegan* version 2.5-1 (Oksanen *et al.*, 2018). Variables were standardized to mean 0 and standard deviation 1 before correlation, as elements differ in measuring units (wt.% and ppm). Similar axis scores on the first PCA axis highlight elements with a similar temporal pattern in VL. It revealed a group of elements with a very similar pattern in VL as the diagenetically stable aluminum (Fig. 4, Al group containing the elements Al_2O_3 , SiO_2 , TiO_2 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , K_2O , P_2O_5 , Ba and Cr). Building on this observation, the VL pattern of each element was correlated with that of the Al group using Spearman's rank correlation, indicating whether an element follows the same variations as those in the Al group.

RESULTS

The LMA is well-bedded with sharp boundaries between beds. Six bundles (five to nine couplets) are observed in the laterally continuous LMA, which can be followed over hundreds of metres, based on variations in the thickness of marls compared to limestones from thick-bedded to thin-bedded (Fig. 3B, red dotted lines). A gradual transition from mudstone to

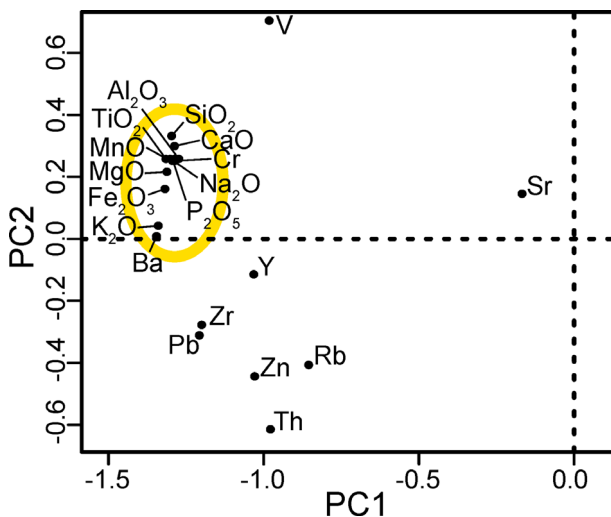


Fig. 4. Principal component analyses of variation in vector length (VL) between trace elements reveals a group (marked with an ellipse) with a pattern similar to the diagenetically stable VL of $\text{TiO}_2/\text{Al}_2\text{O}_3$. This Al group contains the following elements VL with Al_2O_3 : SiO_2 , TiO_2 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , K_2O , P_2O_5 , Ba and Cr.

wackestone in the lower part of the succession to wackestone to packstone in the upper part of the succession is observed and is in line with the description of the Höglint Formation by Munnecke (1997). Overall, the CaCO_3 content increases upward, ranging from 43.7 to 77.8% in marls and from 58.3 to 89.4% in limestones, although the increase is more pronounced in the marl (Fig. 3B). The difference in CaCO_3 content between limestones and marls is more pronounced in the lowermost and uppermost parts of the succession (Fig. 3B). Bed thickness and CaCO_3 content show no relation ($r = 0.07$), while Al_2O_3 and TiO_2 are highly correlated ($r = 0.995$) (Fig. 3A and B). The VL of $\text{TiO}_2/\text{Al}_2\text{O}_3$ and bed thickness correlate by $r = 0.19$, and VL of $\text{TiO}_2/\text{Al}_2\text{O}_3$ and ratio of bed thickness by $r = -0.08$ (compare Fig. 3B).

Principal component analysis reveals similar variations in VL as $\text{TiO}_2/\text{Al}_2\text{O}_3$ for most elements (Fig. 4) which are further referred to as the Al group. Elements fitting into the aragonite lattice (Zn, Ca, Pb, Sr and Ba; Fig. 5) show weak correlations of VL with elements from the Al group, except for CaO and Ba which are also associated with calcite or clay minerals, respectively (Fig. 5). Elements grouped as the incompatible or unassigned elements (V, Cr, Th, Y, Zr, Pb and Rb; Fig. 5) have, except for Cr, weaker correlation of VL with elements from the Al group (Fig. 5). Vector lengths of elements bound to clay minerals (P, Si, Al, Fe, Ti, Mn, Mg, Ba, Na and K; Fig. 5) and/or calcite (Fe, Mn, Mg, Zn and Ca; Fig. 5) correlate by $r > 0.9$ (Fig. 5), although ratios of Al_2O_3 and elements from clay minerals do not correlate.

INTERPRETATION

The LMA at Lickershamn (Höglint Formation) represents deeper shelf deposits based on field and thin section observations. Riding & Watts (1991) assumed *ca* 40 m water depth. Based on the absence of components that indicate the photic zone, as well as the dominance of mudstone and smaller grain size of reef debris of a maximum of few millimetres, a similar or deeper water depth is interpreted. The change up-section from mudstones and wackestones to packstones represents a shallowing upward sequence. A diagenetic origin is identified based on: (i) the good correlation of diagenetically stable elements ($\text{TiO}_2/\text{Al}_2\text{O}_3$; Fig. 3A), which imply a steady composition of terrigenous

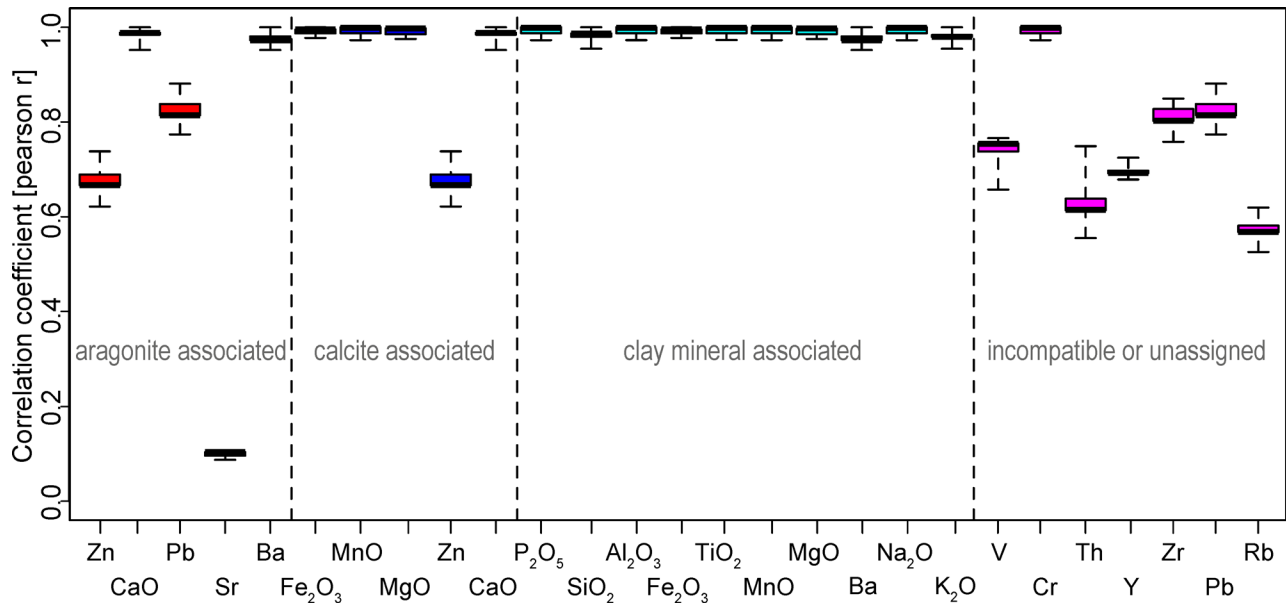


Fig. 5. Variation in vector length (VL) of each trace element were correlated with each trace element from the Al group.

material (Westphal *et al.*, 2008); and (ii) the similar variation in VL of elements bound in clay minerals or calcite, which imply a similar process steering CaCO_3 content and the concentration of trace elements (Fig. 5). Variations in VL of Zn do not correlate with the variation in VL of the Al group. Omitting Zn's four outliers from the measured concentration restores a good fit of the variation in this element's VL to the Al group (Fig. 5). Authigenic sphalerite (ZnS) formation as in the underlying Lower Visby Formation (Spjeldnaes, 2002; Nohl & Munnecke, 2019) or reworking of its deposits can explain the peaks in Zn concentration.

Vector lengths of $\text{TiO}_2/\text{Al}_2\text{O}_3$ with the VL of elements from aragonite correlate by $r = 0.8$ (Pb) and by $r = 0.1$ (Sr). This suggests a loss of Sr during aragonite dissolution. The incompatible or unassigned elements (for example, V, Cr and Th; compare Fig. 5 and Table 1) show large variations. Except for Cr and Th, they are soluble in reducing conditions based on the ionic potential. The distribution of elements not bound to clay minerals or calcite, which are soluble (i.e. with an ionic potential below 3.5 or above 8.5; for example, Sr, V and Pb, see Table 1), seems to be altered by differential diagenesis (Fig. 5). Possible uncertainties, such as measurement precision (link to data provided after the *Conclusions*), may affect

individual elements, but the data is treated further by rank correlation and the uncertainty in measurement will be constant for individual elements.

The combination of VL and CaCO_3 contents in marl and limestone allows assignment of the theoretical scenarios, cases I to IV (Fig. 2), to the patterns observed in the case study. Case 0 does not appear since the terrigenous compound seems stable based on the high correlation of Al_2O_3 and TiO_2 ($r = 0.995$). Trends in variation of VL and CaCO_3 content were interpreted as follows (Fig. 6). The lower part (until 3.9 m height = sample 29) of the section shows variations in VL and a general increase in CaCO_3 . The amount of aragonite varied, but calcite showed minor variations which are inverse to terrigenous material (corresponding to the theoretical cases IIa,b). This shallowing upward trend continues until rather steady conditions begin without variations in VL or CaCO_3 content (I, until 5.1 m height = sample 37). Above (until 6.6 m height = sample 47), there was less aragonite input compared to calcite as only the CaCO_3 content in marls and the VL vary (IVa,b). The low aragonite input is also reflected in the relatively small VL. The dominance of variation in calcite input can be followed up-section (IIIb, until 7.0 m height = sample 50) until a pronounced decrease in aragonite input disturbed

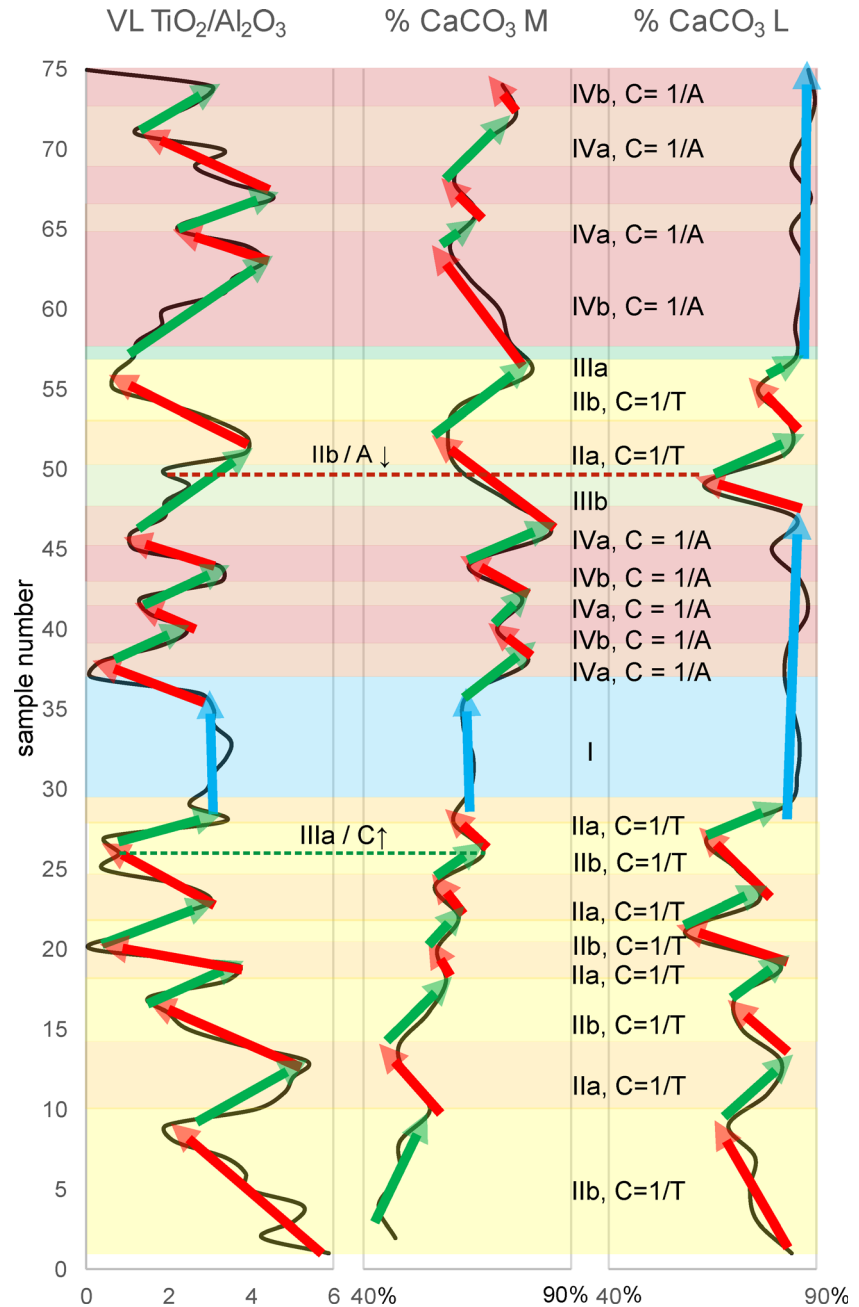


Fig. 6. Trends in calcite and aragonite input (compare case I to IV in Fig. 2) derived from variations in VL of $\text{TiO}_2/\text{Al}_2\text{O}_3$, CaCO_3 content in marl (CaCO_3 M) and CaCO_3 content in limestone (CaCO_3 L). The Y axis was equally spaced by sample number to illustrate only the intensity of CaCO_3 redistribution. Blue arrows indicate stable values, red arrows pointing left indicate decline and green arrows pointing right indicate increase in the obtained values.

the VL trend (IIb). A short interval of variation in the input of aragonite and slight variation in calcite in a pattern reverse to terrigenous material follow (IIa,b, until 8.1 m height = sample 56), before the calcite is dominant again (IVa,b, until 11.3 m height = sample 75). The increase in CaCO_3 alongside the dominant influence of calcite on the pattern of VL and CaCO_3 in the upper part of the section fit the shallowing upward trend of the Högklint Formation (Munnecke, 1997; Watts & Riding, 2000).

DISCUSSION

Identification of (non-)variations in aragonite and calcite input

The importance of shallow diagenetic CaCO_3 redistribution (differential diagenesis) in the formation of LMA has been shown for various depositional environments and geological periods (e.g. Westphal *et al.*, 2015; Nohl & Munnecke, 2019; Nohl *et al.*, 2019; Su *et al.*, 2020).

In the absence of variations in the composition of terrigenous material, variations in calcite and aragonite input are still possible but will not be detectable in the ratio of diagenetically inert elements such as Ti and Al (Westphal *et al.*, 2008). However, VL between ratios of diagenetically inert elements can be used to detect these variations as the intensity of diagenetic overprint, as presented in this case study (Fig. 6) and provides information on diagenetic condensation in marl affecting, for example, bed thickness, and the concentration of major and trace elements. Vector length can differentiate between periods of stable conditions (case I) and original variations in CaCO_3 input (cases II, III and IV; Fig. 2). The method is supported by similar variations of VL in all elements incorporated into calcite or clay minerals which show the same VL pattern as the diagenetically inert $\text{TiO}_2/\text{Al}_2\text{O}_3$, and the mismatch of soluble elements from aragonite (Fig. 5). This means that calcite and clay are not affected by this shallow diagenetic process (Munnecke & Samtleben, 1996; Westphal *et al.*, 2008), but aragonite is dissolved and its soluble elements (for example, Sr), which cannot be incorporated into calcite, diffuse together with soluble incompatible or unassigned elements (for example, V and Th; Fig. 5 and compare Table 1). This also supports the assumption of the model of differential diagenesis, stating that CaCO_3 is redistributed owing to aragonite dissolution and reprecipitation as calcite. Thus, the distribution of incompatible elements (for example, V and Th; Fig. 5 and see Table 1) can be altered by CaCO_3 redistribution (Thomson *et al.*, 1993; De Lange *et al.*, 1994) in the shallow subsurface (Munnecke & Samtleben, 1996), or by the element's solubility, which depends on the redox conditions. It is possible that CaCO_3 is redistributed even earlier, in the oxic zone, associated with aerobic decay of organic material. However, sulphate reduction has been reported as the main process initiating CaCO_3 redistribution (Krumins *et al.*, 2013) and, in the case study, the elements fit the predictions on solubility for the shallow anoxic zones (Table 1; Fig. 5). The incompatible elements and elements bound to aragonite with high solubility show different patterns of VL compared to the supposedly diagenetically stable Al group (Fig. 5). On the other hand, elements bound to calcite, clay minerals or incompatible elements with low solubility show the same vector length curve, i.e. the same difference between marl and limestone, as the Al group (Figs 4 and 5). This

suggests a differentially opened or closed reaction zone depending on: (i) source, i.e. incompatible elements or chemical bonding to aragonite, calcite, clay minerals; and (ii) on ionic potential which steers an ion's solubility. Such partly closed reaction zones have also been suggested for the deep diagenetic model of diagenetic bedding (Brand & Veizer, 1980; Ricken, 1986) and are supported by results in this study. This is in opposition to studies either interpreting an open system (e.g. Wheeley *et al.*, 2008) or assuming a closed system (e.g. Munnecke *et al.*, 2001).

Research on the relative abundance of aragonite and calcite in (precursor) sediments has a long history, but previous approaches mainly focussed on specific types of macroscopic sedimentary grains (Cherns & Wright, 2000; Nohl *et al.*, 2019) and therefore did not assess the mud fraction of the precursor sediment. Other approaches to reconstructing the initial sediment composition of LMA were limited in that they excluded aragonite as a compound of the precursor sediment in the calculations (Ricken, 1986), or in terms of stratigraphic resolution as the averages over several beds are taken (Munnecke & Westphal, 2005). The approach suggested by Munnecke (1997) and Munnecke *et al.* (2001) using ternary plots proposes that the precursor sediment composition can be reconstructed using carbonate content and bed thickness ratio of marls and limestones. However, this method is limited by its dependence on bed thickness, which is easily altered in less cemented marls depending on the depth of burial and the resistance of embedded components to lithostatic stress. It further dismisses the possibility of an at least partly open diagenetic system, as suggested *i.a.* by the massive loss of Sr in originally aragonite-rich sediments (Flügel & Fenninger, 1966). In summary, none of the existing approaches to reconstructing the original composition of the precursor sediment of LMA is suitable for the quantification of absolute abundance and dissolution of aragonite or the extent of its reprecipitation. The VL approach has four advantages since: (i) it includes all main compounds of the precursor sediment (skeletal grains or mud); (ii) it does not involve bed thickness which is easily altered and depends on depth of burial and the resistance of components to lithostatic stress; (iii) it provides a better stratigraphic resolution which can even be employed to identify a homogeneous precursor sediment; and (iv) it can gauge to what

extent the system was closed or open by comparing the similarity between the VL curves of diagenetically mobile and immobile elements.

Phase of non-variation in sediment input

A frequently raised question concerns the trigger of the change between limestone and marl if the precursor sediment was homogeneous. In addition to studies showing the possibility of self-organization (Hallam, 1986; Böhm *et al.*, 2003), L'Heureux (2018) demonstrated in computer simulations the possibility of a self-organized oscillating pattern that 'jumps' when all aragonite is dissolved in the lowest part of the dissolution zone; these results further indicate that in order to preserve environmental changes, which may potentially be astronomically forced, in the resulting lithology, these changes have to reach a large enough intensity to alter the self-organized oscillating pattern. In other words, differential diagenesis is a self-organized geochemical system, which can in some cases be influenced, but not controlled by an external driver (Wang & Budd, 2016). Within other disciplines self-organized processes, such as Liesegang rings in geochemistry, are well-known and accepted (Böhm *et al.*, 2003; Wang & Budd, 2016), but their recognition in carbonate sedimentology is scarce.

Westphal *et al.* (2008) defined the diagenetic dilemma stating that in the absence of variation in all measurable parameters an environmental cause cannot be excluded since it might concern a yet undetected or unmeasured proxy. Yet, if all known proxies do not show a difference between limestones and marls (other than related to CaCO_3 redistribution), a primary origin cannot be demonstrated. According to L'Heureux (2013, 2018) and Wang & Budd (2016), a relatively high signal-to-noise-ratio is needed to influence the geochemical self-organized oscillating process by an external (for example, environmental) signal. Several studies provide examples of substantially different sediment input, for example, coarse-grained storm deposits and fine-grained background sedimentation, to be combined into one limestone bed (e.g. Kent, 1936; Munnecke & Samtleben, 1996; Nohl *et al.*, 2019), representing measurable strong differences. Nevertheless, lithification does not follow this strong environmental signal. Following the law of parsimony, the existence of a 'hidden signal', which is not detectable at present and which is strong

enough to change the self-organized oscillating process, can be rejected at the current state of knowledge.

IMPLICATIONS OF THE VECTOR LENGTH APPROACH

The VL approach offers the possibility to test the intensity of diagenetic overprint for LMA. Where variations in VL give the same pattern for elements bound to calcite or clay minerals, the VL can be used to test for cyclicity in CaCO_3 input (calcite and aragonite). As such, it offers an additional way of considering diagenetic effects on LMA used for cyclostratigraphic analyses that include the development of a robust mechanistical understanding of controlling climatic and environmental controls on the studied signal, making differential diagenesis potentially useful for cyclostratigraphic analyses. The different theoretical cases I to IV (Fig. 2) help to describe the trends observed in VL and CaCO_3 content and, thus, to identify distinct phases of CaCO_3 input a studied succession (cases I to IV, as well as the variations therein), even if the terrigenous material was stable. Still, the studied example reveals no correlation of bed thickness, bed thickness ratio between limestones and marls, bundles, CaCO_3 content, ratio of trace elements and VL (Fig. 3B). This suggests a limitation for the use of couplets or bundles from diagenetically produced or altered LMA for cyclostratigraphic analyses. In the Lickersham case study, VL are probably the best detector of palaeoenvironmental changes.

CONCLUSIONS

The vector length (VL) between trace element ratios reveal primary variations in the sedimentary input of aragonite and calcite in limestone–marl alternations (LMA) which exhibit a constant ratio of diagenetically inert elements. As such, the VL approach also offers a solution to the diagenetic dilemma and can be used to test LMA for diagenetic overprint. The VL approach highlights that the higher the original aragonite content is in the precursor sediment, the stronger is the geochemical alteration during shallow diagenesis. Although a higher original aragonite content means that sedimentary structures are more likely to be preserved, since the potential to increase limestone bed thickness increases,

and therefore prevents compaction of a larger part of the succession. This means that VL provides a measure of diagenetic condensation in marl compared to limestone. The method further offers the possibility to test variations in aragonite and calcite input determined by the VL approach for potential astronomical forcing. The studied Lickershamn case study suggests that LMA can form by differential diagenesis with and without primary differences. The lacking correlation of bed thickness, CaCO_3 content and trace element ratios indicate that lithological patterns (for example, bundles) are not suitable for cyclostratigraphic analyses in this case.

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DATA AVAILABILITY STATEMENT

The results of the measurements (.xlsx-file with raw data, .csv-file with VL used for further analysis, .xlsx-file of measurement uncertainty) and the R-script are available via: <https://doi.org/10.6084/m9.figshare.14061431>.

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